

⑫

EUROPEAN PATENT SPECIFICATION

⑬ Date of publication of patent specification: 12.04.89

⑭ Application number: 85306922.7

⑮ Date of filing: 27.09.85

⑯ Int. Cl.⁴: **B 01 J 27/04, C 10 G 47/06,**
C 10 G 49/02, C 10 G 45/04,
C 10 G 45/66, C 10 G 45/08

⑰ **Hydrotreating catalysts comprising a supported mixture of a sulfide of a promoter, metal, trivalent chromium and molybdenum or tungsten.**

⑱ Priority: 28.09.84 US 656132

⑲ Date of publication of application:
04.06.86 Bulletin 86/23

⑳ Publication of the grant of the patent:
12.04.89 Bulletin 89/15

㉑ Designated Contracting States:
BE CH DE FR GB IT LI NL

㉒ References cited:
DE-A-2 064 376
US-A-3 856 925
US-A-3 907 705
US-A-4 430 443

㉓ Proprietor: Exxon Research and Engineering
Company
P.O.Box 390 180 Park Avenue
Florham Park New Jersey 07932 (US)

㉔ Inventor: Chianelli, Russell Robert
151 Station Road
Somerville, NJ 08876 (US)
Inventor: Ho, Teh Chung
887 Jason Court
Bridgewater, NJ 08807 (US)
Inventor: Jacobson, Allan Joseph
169 Cedar Lane
Princeton, NJ 08540 (US)
Inventor: Young, Archie Richard, II
18 Franklin Place
Montclair, NJ 07042 (US)

㉕ Representative: Somers, Harold Arnold et al
ESSO Engineering (Europe) Ltd. Patents &
Licences Apex Tower High Street
New Malden Surrey KT3 4DJ (GB)

EP 0 183 353 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Description

This invention relates to supported and promoted catalysts containing a sulphide of trivalent chromium.

5 The petroleum industry is increasingly turning to heavy crudes, resids, coal and tar sands as sources for future feedstocks. Feedstocks derived from these heavy materials contain more sulphur and nitrogen than feedstocks derived from more conventional crude oils. These feeds therefore require a considerable amount of upgrading in order to obtain usable products therefrom, such upgrading or refining generally being accomplished by hydrotreating processes which are well-known in the petroleum industry.

10 These processes require the treating with hydrogen of various hydrocarbon fractions, or whole heavy feeds, or feedstocks, in the presence of hydrotreating catalysts to effect conversion of at least a portion of the feeds, or feedstocks to lower molecular weight hydrocarbons, or to effect the removal of unwanted components, or compounds, or their conversion to innocuous or less undesirable compounds. Hydrotreating may be applied to a variety of feedstocks, e.g., solvents, light, middle, or heavy distillate
15 feeds and residual feeds, or fuels. In hydrotreating relatively light feeds, the feeds are treated with hydrogen, often to improve odor, color, stability, combustion characteristics, and the like. Unsaturated hydrocarbons are hydrogenated. Sulfur and nitrogen are removed in such treatments. In the hydrodesulfurization (HDS) of heavier feedstocks, or residua, the sulfur compounds are hydrogenated and cracked. Carbon-sulfur bonds are broken, and the sulfur for the most part is converted to hydrogen sulfide
20 which is removed as a gas from the process. Hydrodenitrogenation (HDN), to some degree also generally accompanies hydrodesulfurization reactions. In the hydrodenitrogenation of heavier feedstocks, or residua, the nitrogen compounds are hydrogenated and cracked. Carbon-nitrogen bonds are broken, and the nitrogen is converted to ammonia and evolved from the process. Hydrodesulfurization, to some degree also generally accompanies hydrodenitrogenation reactions. In the hydrodesulfurization of relatively heavy
25 feedstocks, emphasis is on the removal of sulfur from the feedstock. In the hydrodenitrogenation of relatively heavy feedstocks emphasis is on the removal of nitrogen from the feedstock. Albeit, hydrodesulfurization and hydrodenitrogenation reactions generally occur together, it is usually far more difficult to achieve effective hydrodenitrogenation of feedstocks than hydrodesulfurization of feedstocks.

Catalyst precursors most commonly used for these hydrotreating reactions include materials such as
30 cobalt molybdate on alumina, nickel on alumina, cobalt molybdate promoted with nickel, nickel tungstate, etc. Also, it is well-known to those skilled in the art to use certain transition metal sulfides such as cobalt and molybdenum sulfides and mixtures thereof to upgrade oils containing sulfur and nitrogen compounds by catalytically removing such compounds in the presence of hydrogen, which processes are collectively known as hydrotreating or hydrotreating processes, it being understood that hydrotreating also includes
35 some hydrogenation of aromatic and unsaturated aliphatic hydrocarbons. Thus, U.S. Patent No. 2,914,462 discloses the use of molybdenum sulfide for hydrodesulfurizing gas oil and U.S. 3,148,135 discloses the use of molybdenum sulfide for hydrotreating sulfur and nitrogen-containing hydrocarbon oils. U.S. 2,715,603, discloses the use of molybdenum sulfide as a catalyst for the hydrogenation of heavy oils. Molybdenum and tungsten sulfides have other uses as catalysts in reactions such as hydrogenation,
40 methanation and water gas shift.

In general, with molybdenum and other transition metal sulfide catalysts as well as with other types of catalysts, higher catalyst surface areas result in more active catalysts than similar catalysts with lower surface areas. Thus, those skilled in the art are constantly trying to achieve catalysts that have higher surface areas. More recently, it has been disclosed in U.S. Patent Nos. 4,243,553, and 4,243,554 that
45 molybdenum sulfide catalysts of relatively high surface area may be obtained by thermally decomposing selected thiomolybdate salts at temperatures ranging from 300—800°C in the presence of essentially oxygen-free atmospheres. Suitable atmospheres are disclosed as consisting of argon, a vacuum, nitrogen and hydrogen. In U.S. 4,243,554 an ammonium thiomolybdate salt is decomposed by heating at a rate in excess of 15°C per minute, whereas in U.S. 4,243,553, a substituted ammonium thiomolybdate salt is
50 thermally decomposed at a very slow heating rate of from about 0.5 to 2°C/min. The processes disclosed in these patents are claimed to produce molybdenum disulfide catalysts having superior properties for water gas shift and methanation reactions and for catalyzed hydrogenation or hydrotreating reactions.

Catalysts comprising molybdenum sulfide in combination with other metal sulfides are also known. Thus, U.S. Patent No. 2,891,003 discloses an iron-chromium combination for desulfurizing olefinic gasoline fractions; U.S. 3,116,234 discloses Cr-Mo and also Mo with Fe and/or Cr and/or Ni for HDS; U.S. 3,265,615
55 discloses Cr-Mo for HDN and HDS; U.S. 3,245,903 discloses Fe-Mo and Fe-Co-Mo for lube oil refining; U.S. 3,459,656 discloses Ni-Co-Mo for HDS; U.S. 4,108,761 discloses Fe-Ni-Mo for HDN and U.S. 4,171,258 discloses Fe-Cr-Mo for HDS with steam.

This invention relates to a process for the preparation of supported catalysts comprising a supported
60 mixture of a sulfide of (i) trivalent chromium, (ii) molybdenum and/or tungsten, and (iii) at least one metal selected from (a) Ni, Co, Mn, Cu, Zn, (b) a mixture thereof and (c) a mixture thereof with Fe, the supported species prepared by such process, and to the use of such supported catalysts for hydroprocessing processes, particularly hydrotreating. Thus, the catalytic metals present in a catalyst of this invention must include at least three metals. They are (i) trivalent chromium, (ii) Mo, W or mixture thereof and (iii) at least
65 one of said promoter metals.

EP 0 183 353 B1

More particularly, this invention relates to the preparation and use of supported catalysts useful for hydroprocessing processes such as hydrotreating wherein said catalysts are formed by heating, at elevated temperature, in the presence of sulfur and under oxygen-free conditions, a composite of a support material and one or more precursors comprising a mixture of (i) a hydrated oxide of trivalent chromium and (ii) a thiometallate salt of the general formula $(ML)(Mo,W_{1-y}S_4)$ wherein M is one or more divalent promoter metals selected from (a) Ni, Co, Mn, Cu, Zn, (b) a mixture thereof and (c) a mixture thereof with Fe, wherein y is any value ranging from 0 to 1, and wherein L is one or more, neutral, nitrogen-containing ligands at least one of which is a chelating polydentate ligand. The total denticity of said ligands will generally be about six. Since M can be a mixture of E and at least one additional promoter metal, it will be appreciated that if the supported catalyst species of this invention contains iron, then at least one additional promoter metal must also be present.

In a preferred embodiment ligand L will have a denticity of six and will be three bidentate or two tridentate chelating amines and the oxygen-free conditions will comprise a gaseous mixture of hydrogen and hydrogen sulfide. Some of the catalysts of this invention have hydrotreating or hydrosulfiding activities substantially greater than that of conventional hydrotreating catalysts such as those prepared from cobalt molybdate on alumina, even though their surface areas are not as high.

Hydroprocessing catalyst is meant to include catalysts useful for any process that is carried out in the presence of hydrogen, including, but not limited to, hydrocracking, hydrodenitrogenation, hydrodesulfurization, hydrogenation of aromatic and aliphatic unsaturated hydrocarbons, methanation, water gas shift reactions, etc. These reactions include hydrotrating and hydrosulfiding reactions, the difference generally being thought of as more of a difference in degree than in kind, with hydrotreating conditions being more severe than hydrosulfiding conditions.

The precise nature and composition of the catalyst species that is formed as a result of heating the composite of precursor and support material in the presence of sulfur and under oxygen-free conditions is not known. However, the composition of the corresponding unsupported, bulk catalyst species is known.

Unlike that of the present invention, however, the unsupported, bulk catalysts differ from the supported catalyst species defined herein in that the catalyst species of this invention achieve superior utilization of the catalytic material.

The corresponding bulk, unsupported catalyst species are unique in that they comprise a mixture of (i) a sulfide of at least one promoter metal selected from (a) Ni, Co, Mn, Cu, Zn (b) a mixture thereof and (c) a mixture thereof with Fe, (ii) amorphous sulfide of trivalent chromium and (iii) microcrystallites of metal sulfide of a metal selected from a molybdenum, tungsten and a mixture thereof.

Electron microscope and other analytical techniques have revealed that the size of the molybdenum and/or tungsten microcrystallites present in the corresponding bulk, unsupported catalyst species will generally have dimensions less than about 0.1 microns (μm) by 0.01 microns (μm). In a preferred embodiment the microcrystallite sizes will be less than about 0.05 microns (μm) by 0.01 microns (μm) and still more preferably less than 0.015 microns (μm) by 0.005 microns (μm).

The bulk, unsupported species referred to above were analyzed using X-ray diffraction (XRD). Those skilled in the art are well-acquainted with this technique in which a monochromatic X-ray beam impinges on the sample. Samples of the catalysts were ground to a fine powder and packed into an aluminum tray with a cylindrical recess 25 mm in diameter and 1 mm in depth. The top surface of the sample was flat and co-planar with the top of the aluminium tray after this preparation. Measurements were made in ambient atmosphere using a Siemens D500 X-ray diffractometer in 0-2 θ reflection (Bragg-Brentano) geometry. The incident X-ray beam was taken from a fixed anode copper target with a wavelength of 1.54178 Å ($1\text{Å}=10^{-10}\text{ m}$). The diffracted beams were monochromated using a graphite monochromator to minimize fluorescence and were detected using a proportional counter detector. Data were collected by stepping the detector in angular increments of 0.02° 2 θ and counting at each step for two seconds.

The corresponding bulk, unsupported catalyst species used as hydrotreating catalysts were analyzed using XRD both fresh, that is right after formation, and after being on stream for three days. There was no discernable difference in the X-ray diffraction patterns between the fresh and used catalysts. The diffraction patterns obtained were consistent with MoS_2 microcrystallites of the size observed by the electron microscope. The X-ray diffraction patterns all contained a broad peak between approximately 10 and 15° 2 θ which is indicative of stacks of MoS_2 crystallites with a stack number of about 4. There was no evidence in the X-ray diffraction (XRD) pattern for any crystalline chromium sulfide phase.

Bulk, unsupported catalyst species were examined in an electron microscope having a 4Å ($4\times 10^{-10}\text{ m}$) point-to-point resolution at a magnification of 680,000 \times . Examination of micrographs of these compositions revealed many lines 6.2 Å ($6.2\times 10^{-10}\text{ m}$) apart and generally not more than 150 Å ($15\times 10^{-9}\text{ m}$) in length. It is well known in the art (see for example R. R. Chianelli, International Reviews in Physical Chemistry, (1982), 2(127-165) that such lines with the 6.2 Å ($6.2\times 10^{-10}\text{ m}$) spacings are characteristic of MoS_2 . MoS_2 occurs in layers which are seen to be highly disordered and occurring singly or stacked but in the micrograph the degree of stacking is generally not more than eight stacks and usually not more than four stacks. The Cr_2S_3 phase was observed to be completely amorphous. In some cases a small amount of crystalline Cr_2S_3 phase was detected, but only as a minority phase, less than about 5%. The predominant material which is the catalytically active composition of the bulk catalyst species of Jacobson et al. is a

EP 0 183 353 B1

mixture of (a) microcrystalline MoS_2 , WS_2 or mixture thereof, (b) amorphous Cr_2S_3 and (c) a sulfide of at least one promoter metal.

In one method of preparing the supported catalyst species of this invention, a slurry of precursor material is incorporated with a pre-selected quantity of refractory inorganic oxide support material, preferably a particulate mass of said support, with a resulting composite then dried and the dried, particulate, composite then heated in an oxygen-free atmosphere in the presence of sulfur or sulfur-bearing compound at elevated temperature to form the catalyst species of this invention. A sufficient amount of the precursor salt or salts is composited with the support so that prior to, or at the time that the composite of support and precursor material is heated in the presence of sulfur and hydrogen, generally from about 10 weight percent to about 25 weight percent of the salt, expressed as weight of MoO_3 or WO_3 on an ignition loss free basis, will be present on the support. The supported catalyst species of this invention are highly active and selective as hydrotreating catalysts.

The catalyst support will typically be a particulate, porous inorganic refractory oxide in the form of beads, pills, pellets, sieved particles, extrudates, or the like in dry or solvated state which is contacted with a slurry of precursor. Alternatively, the supported catalysts species of this invention are formed by forming the precursor in the presence of a slurry of colloidal or non-colloidal particles of support material. Typical support materials include alumina, diatomaceous earth, zeolite, silica, activated carbon, magnesia, zirconia, boron, chromia, titania and the like. A preferred support for the practice of the present invention is one having a surface area of more than $50 \text{ m}^2/\text{g}$, preferably from about 100 to $300 \text{ m}^2/\text{g}$.

As hereinbefore stated, the catalysts of this invention may be prepared from a composite of inorganic refractory metal oxide support material and one or more precursors. The precursors will comprise a mixture of (i) a hydrated oxide of trivalent chromium and (ii) a thiometallate salt of the general formula $(\text{ML})(\text{Mo}_y\text{W}_{1-y}\text{S}_4)$ wherein M is one or more divalent promoter metals selected from (a) Ni, Co, Mn, Cu, Zn, (b) mixtures thereof and (c) mixtures thereof with Fe, wherein y is any value ranging from 0 to 1 and L is one or more neutral, nitrogen-containing ligands at least one of which is a chelating polydentate ligand. The total denticity of the ligands used to form the precursor compound will be about six.

If desired, more molybdenum and/or tungsten sulfide may be incorporated into the precursor, and concomitantly the composition of this invention, by also including in the precursor mixture a thiometallate salt of the general formula $(\text{L}')(\text{Mo}_y\text{W}_{1-y}\text{S}_4)$ wherein y is as above and L' is the conjugate acid of one or more ligands, L, with a charge sufficient to balance the dinegative charge of the thiometallate anion. In such a case the precursor will comprise a mixture of (i) a hydrated oxide of trivalent chromium, (ii) a thiometallate salt containing the desired divalent promoter metal of the formula $(\text{ML})(\text{Mo}_y\text{W}_{1-y}\text{S}_4)$ and (iii) a thiometallate salt of the formula $(\text{L}')(\text{Mo}_y\text{W}_{1-y}\text{S}_4)$.

The divalent promoter metal may be a single metal such as Ni in which case the promoter metal containing thiometallate salt would have the formula $(\text{NiL})(\text{Mo}_y\text{W}_{1-y}\text{S}_4)$. Alternatively the promoter metal may be a mixture of two or three promoter metals. For the case of two promoter metals, such as Ni and Co, the thiometallate salt would have the formula



wherein $0 < a < 1$. In the case of three promoter metals such as Ni, Co and Fe, the thiometallate salt would have the formula of the form



wherein $0 < a, b$ and $c < 1$ and $a+b+c=1$.

Ligand L will be one or more neutral, nitrogen containing ligands wherein at least one of said ligands is a multidentate chelating ligand wherein the total denticity of the ligands adds up to six. The ligand chelates the divalent promoter metal cation to form a chelated divalent promoter metal cation $[\text{ML}]^{2+}$. Thus, the metal sulfide anion $(\text{Mo}_y\text{W}_{1-y}\text{S}_4)^{2-}$ will be ionically bound to the chelated divalent promoter metal cation $[\text{ML}]^{2+}$. By neutral is meant that the ligand itself does not have a charge. In its conjugate acid form the ligand forms a chelating cation $[\text{L}']^{2+}$ which is ionically bound to the metal sulfide anion.

Those skilled in the art know that the term "ligand" is used to designate functional coordinating groups which have one or more pairs of electrons available for the formation of coordinate bonds. Ligands that can form more than one bond with a metal ion are called polydentate while ligands that can form only one bond with a metal ion are called monodentate. Monodentate ligands are not capable of forming chelates. Hence, if one uses one or more species of monodentate ligands in the precursor molecule, then one must also use more than one polydentate chelating ligand. Preferably L will be one or more polydentate chelating ligands. The total denticity of the ligand species comprising L will be six. Thus, L will be three bidentate ligands, two tridentate ligands, a mixture of a bidentate and a quadridentate ligand, a hexadentate ligand or a mixture of a polydentate ligand with monodentate ligands as long as the combination has a total denticity of six. As has heretofore been stated, it is preferred to use chelating bidentate and tridentate alkylamine ligands. In general, the ligands useful in this invention include alkyl and aryl amines and nitrogen heterocycles. Illustrative but non-limiting examples of ligands useful in the catalyst precursors of this invention are set forth below.

Monodentate ligands will include NH_3 as well as alkyl and aryl amines such as ethylamine, dimethyl amine, o-phenylene diamine and nitrogen heterocyclic amines such as pyridine, etc. Useful chelating bidentate amine ligands are illustrated by ethylenediamine, 2,2'-bipyridine, o-phenylene diamine, tetramethylethylenediamine and propane-1,3 diamine. Similarly, useful chelating tridentate amine ligands are represented by terpyridine and diethylenetriamine while triethylenetetramine is illustrative of a useful chelating quadridentate amine ligand. Useful chelating pentadentate ligands include tetraethylene pentamine while sepulchrate (an octazacryptate) is illustrative of a suitable chelating hexadentate ligand. As a practical matter it will be preferred to use chelating, polydentate alkyl amines. Illustrative, but not limiting examples of alkyl amines that are useful in the catalyst precursor of this invention include ethylenediamine, diethylenetriamine, and tetraethylenetetramine. It is particularly preferred to use bidentate and tridentate alkyl amines such as ethylenediamine, (en), and diethylenetriamine, (dien).

The conjugate acid of ligand L, referred to as L' , will have a charge sufficient to balance the dinegative charge of the thiometallate anion. For example, if L is ethylenediamine (en), L' will be $[\text{H}_2\text{en}]$ and the corresponding thiomolybdate salt, for example, will be $[\text{H}_2\text{en}]_2(\text{MoS}_4)$. For diethylene triamine, (dien), the corresponding salt will be $[\text{H}_2\text{dien}]_2(\text{MoS}_4)$.

In general, the precursors useful for forming the compositions of this invention may be prepared by mixing a slurry of (i) a hydrated oxide of trivalent chromium $\text{Cr}(\text{OH})_3 \cdot x\text{H}_2\text{O}$, with (ii) one or more of the promoter metal and ligand containing thiometallate salts and, optionally, (iii) one or more thiometallate salts of Mo and/or W containing the conjugate acid of one or more ligands, but no divalent promoter metal. The thiometallate salt is then precipitated onto the slurried particles of hydrated chromium oxide and the precursor is recovered. The hydrated chromium oxide may be freshly precipitated from an aqueous solution of a trivalent chromium salt. Alternatively, the source of hydrated chromic oxide may be colloidal, aqueous suspension of same. In one method of preparation the hydrated chromium oxide will be precipitated from an aqueous solution of trivalent chromium salt by contacting said salt solution with one or more basic amine chelating agents.

Thus, one embodiment a water soluble trivalent chromium compound and divalent metal salt are dissolved in water and hydrated chromium oxide is precipitated by addition of a ligand, L or a mixture of ligands, L. This procedure produces a slurry or suspension of very fine particles of a hydrated oxide of trivalent chromium in the aqueous phase, which also contains some free ligand L, and some of the conjugate acid of the ligand L, L' . When the conjugate acid is a strong acid, that is if the ligand L is a weak base, then a quantity of ammonium hydroxide may be added to precipitate the chromium. The water soluble chromium salt may be any water soluble salt that is convenient to use such as halide, sulfate, nitrate, etc. Sufficient ligand L is added to form the water soluble chelated promoter metal cations $[\text{ML}]^{2+}$. This suspension of hydrated chromium oxide containing $[\text{ML}]^{2+}$ in solution is then mixed with a solution of the thiometallate prepared by dissolving ammonium thiometallate in an excess of the ligand or mixture of ligands. A small amount of water may be added if desired. On mixing the slurry with the thiometallate solution an orange-red colored precipitate of the catalyst precursor forms which is recovered by filtration. This precipitate will be a precursor of a composition of this invention. Any step of this preparation may be done in the presence of a slurry of support material. If the chromia is present in sufficient amount, then the excess will act as all or a portion of the support.

In another embodiment the thiometallate salts $(\text{ML})(\text{Mo}_y\text{W}_{1-y}\text{S}_4)$ and $(\text{L}')(\text{Mo}_y\text{W}_{1-y}\text{S}_4)$ may be prepared separately and mixed separately or together with the hydrated chromium oxide slurry prepared as described above. Again, this may be done in the presence of a slurry of support material. If the chromia is present in sufficient amounts, then the excess chromia will comprise all or a portion of the support.

The salts $(\text{L}')(\text{Mo}_y\text{W}_{1-y}\text{S}_4)$ may generally be prepared by dissolving the ammonium thiometallate in excess of the ligand L. The salt is recovered as a precipitate by addition of water or some other suitable antisolvent such as methanol or acetone. This may, if desired, be done in the presence of a slurry of one or more support materials. Many of the thiometallate salts $(\text{ML})(\text{Mo}_y\text{W}_{1-y}\text{S}_4)$ and methods for preparing them are known in the art. An article by Diemann and Mueller titled Thio and Seleno Compounds of the Transition Metals with d⁰ Configuration published in Coord. Chem. Rev. 10:79—122 provides a review of known promoted thiometallate salts useful for preparing the compositions of this invention. In general, these salts may be prepared by mixing an aqueous solution of ammonium thiomolybdate and/or thiotungstate with an aqueous solution of the chelated promoter metal cation $[\text{ML}]^{2+}$ which results in the formation of the salt as a precipitate which is readily recovered. The chelated promoter cation is easily formed by, for example, mixing an aqueous solution of one or more water soluble promoter metal salts with the ligand. The water soluble salt may be any water soluble salt that is convenient to use such as a halide, sulfate, perchlorate, acetate, nitrate, etc. Alternatively, an aqueous solution of ammonium thiomolybdate and/or tungstate may be mixed with an aqueous solution of the chelated promoter metal salt or the salt can be added to the ligand and dissolved into the solution of thiomolybdate and/or thiotungstate.

The compositions or catalysts of this invention will be prepared by heating a composite of a suitable inorganic, refractory metal oxide support material and one or more precursors, in an oxygen-free environment and in the presence of sulfur, at a temperature of at least about 200°C for a time sufficient to form the catalyst. Although the sulfur required during the formation of the catalyst may be present in the precursor, it is preferred that the sulfur be present in an amount in excess of that contained in the

EP 0 183 353 B1

precursor. Thus, it is preferred that the composition be formed by heating the precursor in the presence of sulfur or, preferably, in the presence of a sulfur bearing compound. Mixtures of hydrogen and H_2S have been found to be particularly suitable. Preferably the temperature will range between from about 250—600°C, more preferably from about 250—500°C and still more preferably from about 300—400°C. The oxygen-free environment may be gaseous, liquid or mixture thereof.

As discussed previously molybdenum and tungsten sulfide catalysts have many uses, including hydrotreating. Hydrotreating conditions vary considerably depending on the nature of the hydrocarbon being hydrogenated, the nature of the impurities or contaminants to be reacted or removed, and, inter alia, the extent of conversion desired, if any. In general however, the following Table illustrates typical conditions for hydrotreating a naphtha boiling within a range of from about 25°C to about 210°C, a diesel fuel boiling within a range of from about 170°C to 350°C, a heavy gas oil boiling within a range of from about 325°C to about 475°C, a lubricating oil feed boiling within a range of from about 290 to 550°C, or residuum containing from about 10 percent to about 50 percent of a material boiling above about 575°C.

Typical hydrotreating conditions

Feed	Temp., °C	Pressure psig (MPa)	Space velocity V/V/hr	Hydrogen gas rate SCF/B (l/l)
Naphtha	100—370	150—800 (1.03—5.52)	0.5—10	100—2000 (17.8—356.1)
Diesel	200—400	250—1500 (1.72—10.3)	0.5—4	500—6000 (89.0—1068.5)
Heavy gas oil	260—430	250—2500 (1.72—172)	0.3—2	1000—6000 (178.0—1068.5)
Lube oil	200—450	100—3000 (0.69—20.7)	0.2—5	100—10,000 (17.8—1780.9)
Residuum	340—450	1000—5000 (6.89—34.5)	0.1—1	2000—10,000 (356.1—1780.9)

EP 0 183 353 B1

It should be noted that the compositions of this invention are useful catalysts for lubricating oil refining processes where it is desirable to remove oxidation initiating nitrogen compounds from lubricating oil feeds.

The invention will be further understood by reference to the following examples.

5

Example 1

Precursor preparation

Precursor A

A precursor comprising hydrated chromium hydroxide and a nickel promoted thiomolybdate was prepared by dissolving ammonium thiomolybdate into diethylenetriamine (dien) and the resulting dark red solution cooled to 0°C in an ice bath. An aqueous solution of a mixture of chromium and nickel chloride was slowly added, in aliquots, to the dark red solution, with agitation after the addition of each aliquot. An orange precipitate was formed and recovered by vacuum filtration. More specifically, 40 grams of $(\text{NH}_4)_2\text{MoS}_4$ was added to 82 ml of diethylenetriamine (dien) in a one liter flask. Distilled H_2O was used twice to wash off any solution remaining on the sides of the flask. The resulting dark red solution was cooled to 0°C in an ice bath and kept in the bath for the duration of the preparation. In a separate flask 16.52 grams of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and 14.77 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved into a mixture of 250 ml of distilled H_2O and 25 ml of diethylenetriamine to precipitate the hydrated chromium oxide and to chelate the nickel ion. This slurry was allowed to stand for 2—3 hours after which it was slowly added dropwise, to the cold $(\text{NH}_4)_2\text{MoS}_4/\text{dien}$ solution with agitation after each addition keeping the flask as cold as possible, which resulted in a bright orange precipitate being formed. The resulting precipitate-containing mixture was stirred in the ice bath for one half hour after the addition was completed. The ppt was separated out by vacuum filtration through a Buchner funnel. The catalyst precursor product was washed with distilled water, then with ethanol, and dried under vacuum for 16—24 hrs. Eighty three grams of orange colored precipitate, Precursor A, were recovered.

Precursor B

A chromium-nickel thiomolybdate precursor was prepared in a similar manner by dissolving 40 grams of ammonium thiomolybdate into 82 ml of ethylenediamine in a 1 liter flask which was cooled to 0°C in a wet ice bath. In a separate flask 9.98 grams of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 36.72 grams of $\text{Cr}(\text{NO}_3)_3 \cdot 7\text{H}_2\text{O}$ were dissolved in 300 ml of water and 25 ml of ethylenediamine added thereto which resulted in formation of a precipitate. The resulting slurry was allowed to stand for 2—3 hours after which it was then slowly added, dropwise, to the chilled $(\text{NH}_4)_2\text{MoS}_4/\text{en}$ solution, with agitation, which resulted in an orange precipitate. The mixture was then stirred in the ice bath for one half hour and recovered as was the precipitate in the other examples. This product was designated Precursor B.

Precursor C

A chromium-cobalt thiomolybdate catalyst precursor was prepared in a similar manner by dissolving 40 grams of $(\text{NH}_4)_2\text{MoS}_4$ in 82 ml of diethylenetriamine in a one liter flask which formed a dark red solution. The sides of the flask were washed with distilled water and the flask cooled to 0°C in a wet ice bath and kept in the bath for the duration of the experiment. In a separate flask a mixture of 16.52 grams of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and 14.78 grams of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 250 ml of distilled water. To this solution was added 25 ml of dien to form a precipitate. The resulting slurry was allowed to stand for 2—3 hours and then slowly added (dropwise) to the $(\text{NH}_4)_2\text{MoS}_4/\text{dien}$ solution with agitation, which formed a bright orange precipitate. The resulting precipitate/solution was stirred in the ice bath for a half hour after the reaction was completed.

The precipitate was then separated by vacuum filtration and washed with water and ethanol and then dried under vacuum. Eighty-three grams of orange colored solid, Precursor C, were recovered.

50 Precursor D

Another chromium-nickel thiomolybdate catalyst precursor was prepared as follows:

An aqueous suspension of colloidal chromia, 163.1 g, containing 22 wt.% Cr_2O_3 , was dispersed in 400 cm^3 of water, and placed in a 2000 cm^3 flask. With constant agitation, a solution of 14 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 34.6 g of ethylenediamine in 75 cm^3 of water was added to the flask dropwise via a separatory funnel. A purple gel formed, to which a solution of 15.4 g $(\text{NH}_4)_2\text{MoS}_4$ in 100 cm^3 water and 50 cc ethylenediamine was slowly added, dropwise with constant agitation. An orange-red precipitate was formed, characteristic of $\text{Ni}(\text{en})_3\text{MoS}_4$. The resultant precipitate was recovered by vacuum filtration through a Buchner funnel, dried under vacuum at 50°C, producing Precursor D.

60 Precursor E

A chromium-nickel thiotungstate catalyst precursor was prepared in a manner similar to Precursor D except for the following change:

The amount of colloidal chromia suspension was 147.6 g; the nickel solution contained 12.6 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and the precipitating solution consisted of 18.5 g $(\text{NH}_4)_2\text{WS}_4$ in 100 cm^3 water and 50 cm^3 ethylenediamine. This procedure formed Precursor E.

EP 0 183 353 B1

Catalyst preparation

The precursors were pelletized using a 4% aqueous solution of polyvinyl alcohol as a binder. Each pelletized precursor was loaded into a stainless steel reactor and purged for one hour under nitrogen at 100°C and atmospheric pressure. Ten percent of hydrogen sulfide in hydrogen was introduced into the reactor at a rate of 0.75 SCF/hr (21.2 l/hr) for each 10 cm³ of catalyst in the reactor. The temperature in the reactor was then raised to 325°C and held at this temperature for three hours to form a catalyst composition of this invention after which the temperature in the reactor was lowered to 100°C, the H₂S/H₂ gas flow was stopped and the reactor was purged with nitrogen and allowed to cool to room temperature.

Elemental analyses of the catalysts or compositions of this invention formed by sulfiding Precursor A described above are set forth below in wt. %.

Precursor	Cr	Mo	Ni	S	C	H	N
A:	10.34	24.51	12.45	31.93	6.81	1.28	0.11

The catalyst based on Precursor A had been run on oil in a reactor for three days prior to analysis.

Reaction conditions

About 20 g of the catalyst was loaded into a fixed-bed reactor. Hydrotreating was carried out at the conditions set forth below:

Temperature	325°C
Pressure	3.15 MPa
Hydrogen rate	3000 SCF/bbl (534.2 l/l)
LHSV	3.0, 4.0 V/V/hr.

Liquid product was analyzed for total sulfur by X-ray fluorescence and for nitrogen by combustion analysis. The feedstock used was a light catalytic cycle oil (LCCO) that was about 20 wt. % paraffinic having nominal properties set forth in Table 1.

Hydrotreating experiments

In all of these experiments, the results obtained from the catalyst compositions of this invention were compared to results obtained from a commercial hydrotreating catalyst comprising nickel molybdate on γ -Al₂O₃. This catalyst contained 18 percent molybdenum oxide and 3.5 percent nickel oxide supported on gamma alumina. The commercial catalyst was sulfided employing the same procedure used to form the catalysts of this invention, except that the temperature was 360°C for one hour.

The results of these experiments are shown in Tables 2 through 6 and show that the catalysts of this invention are not only useful hydrotreating catalysts but have higher selectivity for hydrodenitrogenation than the commercial nickel molybdate on alumina catalyst.

TABLE 1
LCCO Feed

Gravity (°API)	18.6
Sulfur, wt. %	1.4
Nitrogen, ppm	292

GC Distillation

Wt. %	Temp. °C
5	231
10	251
50	293
70	321
90	352
95	364

EP 0 183 353 B1

TABLE 2
Hydrotreating activity for commercial nickel molybdate on alumina*

	Catalyst hours on stream	% HDS	% HDN
5	49	80.0	32.3
	71	80.8	38.6
	75	80.0	37.6

* LHSV 3.0.

TABLE 3
Hydrotreating activity for catalyst prepared from chromium-nickel thiomolybdate Precursor B prepared with ethylenediamine*

	Catalyst hours on stream	% HDS	% HDN
20	39	79.2	89.1
	57	82.5	91.6
	62	82.5	93.2

* LHSV 4.0.

TABLE 4
Hydrotreating activity of catalyst prepared from cobalt-chromium thiomolybdate Precursor C*

	Catalyst hours on stream	% HDS	% HDN
30	42	70.8	34.6
	46	80.6	35.5
	65	72.7	34.3

* LHSV 4.0.

TABLE 5
Hydrotreating activity for catalyst prepared from a nickel-chromium thiomolybdate Precursor D*

	Catalyst hours on stream	% HDS	% HDN
40	44	51	50.9

* LHSV 3.0.

TABLE 6
Hydrotreating activity for catalyst prepared from nickel-chromium thiotungstate Precursor E*

	Catalyst hours on stream	% HDS	% HDN
50	48	61.7	58.8

* LHSV 3.0.

Example 2

In this experiment, a manganese promoted chromium molybdenum catalyst supported on Cr_2O_3 was prepared. Here, 80.7 g of colloidal chromia suspension, containing 22 wt. % Cr_2O_3 (Nyacol) was diluted to 400 ml, and a solution of 5.1 g $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in 50 ml deionized water added to it, with stirring. Dropwise addition of a solution of 2.6 g $(\text{NH}_4)_2\text{MoS}_4$ in 100 ml water and 25 ml ethylene diamine to the resultant gel, resulted in the formation of the precursor on the surface of the chromia and concomitant precipitation of the composite of precursor and chromia support, which was separated by filtration, washing and drying. Analysis of the dry composite revealed a Cr_2O_3 content of over 60 wt. %.

EP 0 183 353 B1

Pelletizing and sulfiding of the resultant solid yielded a catalyst which, upon testing on LCCO over a period of 46 hrs at an LHSV of 3.5—4.5 produced a K_{HDS} (2nd order) of 2.1 and a K_{HDN} of the same value. The relative HDN vs. HDS reactivity is therefore close to unity.

5 Example 3

A manganese promoted molybdenum catalyst supported on silica was prepared, in the absence of colloidal chromium oxide, employing a procedure similar to that of Example 2. Thus, 48 grams of colloidal SiO_2 (34%) was added to a large three neck flask and diluted to 400 ml with deionized water. To this was added a solution of 2 ml of H_2SO_4 and 5.75 grams of $MnSO_4 \cdot H_2O$ in 50 ml of H_2O . A separate solution was made by dissolving 8.8 grams of $(NH_4)_2MoS_4$ in a mixture of 100 ml of water and 25 ml of ethylenediamine. This solution was added dropwise, with vigorous stirring, to the large flask containing the manganese sulfate and colloidal silica. An orange precipitate resulted. The resulting solids, 33.55 grams, were washed with H_2O and dried at 50°C in a vacuum oven. Analysis of the solids revealed an SiO_2 content of 68.24%.

Pelletizing and sulfiding of the dry solid yielded a catalyst having a K_{HDS} of only 0.65. There was essentially no hydrodenitrogenation activity.

Example 4

A 34 wt. % suspension of colloidal silica, 147 g, was diluted with 100 g of distilled water. A solution of 26.4 g of $Cr(NO_3)_3 \cdot 9H_2O$ in 35 g of distilled water was added to this colloidal suspension. A solution of 25.8 g of $(NH_4)_2MoS_4$ in 100 ml ethylenediamine was added dropwise to the silica suspension with constant agitation, and the stirring continued for 20—30 minutes after all the en solution had been added. A precipitate formed which was filtered and dried in a vacuum oven at 50°C, sulfided as in Example 1 and rescreened to 20/40 mesh (0.84/0.42 mm).

25 Reaction conditions

The same reaction conditions were employed as in Example 1. The results shown in Table 7 were obtained.

TABLE 7
Hydrotreating with supported catalyst

Run length, hrs	% HDS	% HDN
48	36.9	35.3
69	32.1	24.9
140	33.3	25.4

While the desulfurization level is much lower than that achieved with a commercial catalyst (see Table 2, Example 1) the denitrogenation obtained with this supported catalyst is about the same order as with commercial material. This shows that the ratio of HDN/HDS activity of the supported catalyst of this invention is higher than that of commercial catalyst.

Claims

1. A composition of matter comprising a catalyst which comprises a supported mixture of a sulphide of (i) trivalent chromium, (ii) molybdenum, tungsten or a mixture thereof and (iii) at least one promoter metal selected from (a) Ni, Co, Mn, Cu, Zn, (b) a mixture thereof and (c) a mixture thereof with Fe, said catalyst obtained by compositing a preselected quantity of support material with a hydrated oxide of trivalent chromium and one or more precursor salts containing a thiometallate anion of Mo, W or mixture thereof and a cation containing at least one of said promoter metals wherein said promoter metal in said cation is divalent and is chelated by at least one neutral, nitrogen-containing polydentate ligand and heating said composite at an elevated temperature, in the presence of sulphur and under oxygen-free conditions for a time sufficient to form said catalyst.
2. A composition according to claim 1 which contains at least two promoter metals, one of which is Fe.
3. A composition according to either of claims 1 and 2 formed in the presence of excess sulphur.
4. A composition according to any one of the preceding claims wherein said elevated temperature is at least 150°C.
5. A composition according to any one of the preceding claims wherein said support material comprises an inorganic refractory oxide.
6. A composition of matter comprising a supported catalyst prepared by heating at elevated temperature of at least 150°C, in the presence of sulphur and under oxygen-free conditions, a composite of support material and one or more precursors comprising a mixture of (i) a hydrated oxide of trivalent chromium and (ii) a thiometallate salt of the general formula $(ML)(Mo_xW_{1-y}S_4)$ wherein M is one or more divalent promoter metals selected from (a) Ni, Co, Mn, Cu, Zn (b) a mixture thereof and (c) a mixture thereof

EP 0 183 353 B1

with Fe, wherein y is any value ranging from 0 to 1 and wherein L is one or more neutral, nitrogen-containing ligands at least one of which is a chelating polydentate ligand.

7. A composition according to claim 6 formed in the presence of excess sulphur in the form of a sulphur-bearing compound.

5 8. A composition according to either of claims 6 and 7 wherein the ligand L is selected from alkyl amines, aryl amines, nitrogen heterocycles and mixtures thereof.

9. A composition according to any one of claims 6 to 8, wherein said support material comprises one or more inorganic refractory oxides.

10. A composition according to any one of claims 6 to 9 wherein the ligand L comprises an alkyl amine.

10 11. A composition according to any one of claims 6 to 10 wherein said non-oxidising atmosphere comprises a mixture of H_2 and H_2S .

12. A hydroprocessing process comprising contacting a hydrocarbon feed at a temperature of at least $100^\circ C$ and in the presence of hydrogen, with a catalyst comprising a composition according to any one of the preceding claims, said contacting occurring for a time sufficient to hydroprocess at least a portion of
15 said feed.

13. A process according to claim 12 wherein at least a portion of said feed is upgraded.

14. A process according to claim 13 wherein said upgrading comprises hydrotreating.

15. A process for removing nitrogen from a nitrogen-containing hydrocarbon feed which comprises contacting said feed at an elevated temperature of at least $150^\circ C$ and in the presence of hydrogen with a
20 catalyst comprising a composition according to any one of claims 1 to 11, and wherein said feed is contacted with said catalyst for a time sufficient to remove at least a portion of said nitrogen from said feed.

16. A process according to claim 15 wherein the feed is a lubricating oil feed containing nitrogen and sulphur and wherein the oxidation stability of said feed is improved.

17. A process according to any one of claims 12 to 15 wherein said feed comprises a lubricating oil
25 feed.

Patentansprüche

1. Zusammensetzung, die einen Katalysator umfaßt, der eine auf einen Träger aufgebrachte Mischung
30 aus einem Sulfid des (i) dreiwertigen Chroms, (ii) des Molybdäns, Wolframs oder einer Mischung derselben und (iii) mindestens eines Promotormetalls ausgewählt aus (a) Ni, Co, Mn, Cu, Zn (b) einer Mischung derselben und (c) einer Mischung derselben mit Fe enthält, wobei der Katalysator durch Zusammenbringen einer vorbestimmten Menge Trägermaterial mit einem hydratisierten Oxid des dreiwertigen Chroms und einem oder mehreren Vorläufersalzen, die ein Thiometallatanion von Mo, W
35 oder einer Mischung derselben und ein Kation enthalten, das mindestens eines der Promotormetalle enthält, wobei das Promotormetall in dem Kation zweiwertig und durch mindestens einen neutralen stickstoffhaltigen mehrzähligen Liganden chelatisiert ist, und für die Bildung des Katalysators ausreichend langes Erwärmen des Verbundmaterials auf eine erhöhte Temperatur in Gegenwart von Schwefel und unter sauerstofffreien Bedingungen erhalten worden ist.

40 2. Zusammensetzung nach Anspruch 1, die mindestens zwei Promotormetalle enthält, von denen eines Fe ist.

3. Zusammensetzung nach Anspruch 1 oder 2, die in Gegenwart von überschüssigem Schwefel gebildet worden ist.

4. Zusammensetzung nach einem der vorangehenden Ansprüche, wobei die erhöhte Temperatur
45 mindestens 150° ist.

5. Zusammensetzung nach einem der vorangehenden Ansprüche, in der das Trägermaterial ein hitzebeständiges anorganisches Oxid umfaßt.

6. Zusammensetzung, die einen Trägerkatalysator umfaßt, der durch Erwärmen eines Verbundmaterials aus Trägermaterial und einem oder mehreren Vorläufern, die eine Mischung aus (i)
50 einem hydratisierten Oxid des dreiwertigen Chroms und (ii) einem Thiometallatsalz der allgemeinen Formel $(ML)(Mo_yW_{1-y}S_4)$ umfassen, in der M ein oder mehrere zweiwertige Promotormetalle ausgewählt aus (a) Ni, Co, Mn, Cu, Zn, (b) einer Mischung derselben und (c) einer Mischung derselben mit Fe bedeutet, y ein Wert im Bereich von 0 bis 1 ist und L ein oder mehrere neutrale stickstoffhaltigen Liganden bedeutet, von denen mindestens einer ein chelatisierender mehrzähliger Ligand ist, auf eine erhöhte Temperatur
55 von mindestens $150^\circ C$ in der Gegenwart von Schwefel und unter sauerstofffreien Bedingungen hergestellt worden ist.

7. Zusammensetzung nach Anspruch 6, die in der Gegenwart von überschüssigem Schwefel in Form einer schwefeltragenden Verbindung gebildet worden ist.

8. Zusammensetzung nach Anspruch 6 oder 7, in der der Ligand L aus Alkylaminen, Arylaminen,
60 Stickstoffheterocyclen und der Mischungen ausgewählt ist.

9. Zusammensetzung nach einem der Ansprüche 6 bis 8, in der das Trägermaterial ein oder mehrere hitzebeständige anorganische Oxide umfaßt.

10. Zusammensetzung nach einem der Ansprüche 6 bis 9, in der der Ligand L ein Alkylamin umfaßt.

11. Zusammensetzung nach einem der Ansprüche 6 bis 10, in der die nichtoxydierende Atmosphäre
65 eine Mischung aus H_2 und H_2S umfaßt.

EP 0 183 353 B1

12. Wasserstoffbehandlungsverfahren, bei dem ein Kohlenwasserstoffeinsatzmaterial bei einer Temperatur von mindestens 100°C und in Gegenwart von Wasserstoff mit einem Katalysator kontaktiert wird, der eine Zusammensetzung nach einem der vorangehenden Ansprüche enthält, wobei das Kontaktieren ausreichend lange erfolgt, um mindestens einen Teil des Einsatzmaterials zu hydroprozessieren.
13. Verfahren nach Anspruch 12, bei dem mindestens ein Teil des Einsatzmaterials veredelt wird.
14. Verfahren nach Anspruch 13, bei dem die Veredelung die Behandlung mit Wasserstoff umfaßt.
15. Verfahren zur Entfernung von Stickstoff aus einem stickstoffhaltigen Kohlenwasserstoffeinsatzmaterial, bei dem das Einsatzmaterial bei einer erhöhten Temperatur von mindestens 150°C und in Gegenwart von Wasserstoff mit einem Katalysator kontaktiert wird, der eine Zusammensetzung nach einem der Ansprüche 1 bis 11 enthält, und das Einsatzmaterial mit dem Katalysator ausreichend lange kontaktiert wird, um mindestens einen Teil des Stickstoffs aus dem Einsatzmaterial zu entfernen.
16. Verfahren nach Anspruch 15, bei dem das Einsatzmaterial ein Schmieröleinsatzmaterial ist, das Stickstoff und Schwefel enthält, und die Oxydationsstabilität des Einsatzmaterials verbessert wird.
17. Verfahren nach einem der Ansprüche 12 bis 15, bei dem das Einsatzmaterial ein Schmieröleinsatzmaterial umfaßt.

Revendications

1. Composition de matière comprenant un catalyseur qui comprend un mélange, sur support, d'un sulfure (i) de chrome trivalent, (ii) de molybdène, de tungstène ou d'un de leurs mélanges, et (iii) au moins un métal promoteur choisi parmi (a) Ni, Co, Mn, Cu, Zn, (b) un de leurs mélanges, et (c) un de leurs mélanges avec Fe, ledit catalyseur étant obtenu en combinant une quantité, choisie au préalable, de matière de support avec un oxyde hydraté de chrome trivalent et un ou plusieurs sels précurseurs contenant un anion thiométallate de Mo, W ou un de leurs mélanges et un cation contenant au moins l'un desdits métaux promoteurs, ledit métal promoteur présent dans ledit cation étant divalent et étant chélaté par au moins un ligand polydenté neutre, contenant de l'azote, et en chauffant ce composite à une température élevée, en présence de soufre et dans des conditions d'absence d'oxygène, pendant un temps suffisant pour former ledit catalyseur.
2. Composition selon la revendication 1, qui contient au moins deux métaux promoteurs, dont l'un est Fe.
3. Composition selon l'une ou l'autre des revendications 1 et 2, formée en présence d'un excès de soufre.
4. Composition selon l'une quelconque des revendications précédentes, pour laquelle ladite température élevée est au moins égale à 150°C.
5. Composition selon l'une quelconque des revendications précédentes, dans laquelle ladite matière de support comprend un oxyde réfractaire minéral.
6. Composition de matière comprenant un catalyseur sur support, préparé par chauffage à une température élevée, d'au moins 150°C, en présence de soufre et dans des conditions d'absence d'oxygène, d'un composite formé d'une matière de support et d'un ou plusieurs précurseurs comprenant (i) d'un oxyde hydraté de chrome trivalent et (ii) d'un sel qui est un thiométallate de formule générale (ML)(Mo_yW_{1-y}S_x), dans laquelle M représente un ou plusieurs métaux promoteurs divalents, choisis parmi (a) Ni, Co, Mn, Cu, Zn, (b) un de leurs mélanges, et (c) un de leurs mélanges avec Fe, y a n'importe quelle valeur de 0 à 1 et L représente un ou plusieurs ligands neutre(s), contenant de l'azote et dont l'un au moins est un ligand chélateur polydenté.
7. Composition selon la revendication 6, formée en présence d'un excès de soufre sous la forme d'un composé contenant du soufre.
8. Composition selon l'une ou l'autre des revendications 6 et 7, dans laquelle le ligand L est choisi parmi les alkyl amines, les aryl amines, les hétérocycles azotés et leurs mélanges.
9. Composition selon l'une quelconque des revendications 6 à 8, dans laquelle ladite matière de support comprend un ou plusieurs oxydes réfractaires minéraux.
10. Composition selon l'une quelconque des revendications 6 à 9, dans laquelle le ligand L comprend une alkyl amine.
11. Composition selon l'une quelconque des revendications 6 à 10, dans laquelle ladite atmosphère non-oxydante comprend un mélange de H₂ et de H₂S.
12. Procédé d'hydrotraitement comprenant la mise en contact, à une température d'au moins 100°C et en présence d'hydrogène, d'une charge d'hydrocarbures avec un catalyseur comprenant une composition selon l'une quelconque des revendications précédentes, ladite mise en contact se produisant pendant un temps suffisant pour hydrotraiter au moins une partie de ladite alimentation.
13. Procédé selon la revendication 12, dans lequel au moins une partie de ladite alimentation est améliorée et valorisée.
14. Procédé selon la revendication 13, dans lequel ladite amélioration comprend un hydrotraitement (traitement par l'hydrogène).
15. Procédé pour enlever l'azote d'une charge d'hydrocarbures contenant de l'azote, qui comprend la mise de cette charge, à une température élevée, au moins égale à 150°C et en opérant en présence

EP 0 183 353 B1

d'hydrogène, en contact avec un catalyseur comprenant une composition selon l'une quelconque des revendications 1 à 11, et dans lequel ladite charge est mise en contact avec ledit catalyseur pendant un temps suffisant pour enlever au moins une partie dudit azote de ladite charge d'alimentation.

5 16. Procédé selon la revendication 15, dans lequel la charge d'alimentation est une huile lubrifiante contenant de l'azote et du soufre, et dans lequel la stabilité à l'oxydation de ladite charge d'alimentation est améliorée.

17. Procédé selon l'une quelconque des revendications 12 à 15, dans lequel ladite charge d'alimentation comprend une charge pour production d'une huile lubrifiante.

10

15

20

25

30

35

40

45

50

55

60

65